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(54) An Article comprising a pb-free solder having improved mechanical properties.

(57) A Pb-free solder alloy, based on the Sn-In-Zn system (exemplarily 86:5:9 weight %), is disclosed. Composition can have a melting temperature in the range  $183^{\circ}\text{C} \pm 10^{\circ}\text{C}$  and thus can be readily substituted for conventional 40 Pb - 60 Sn solder. The novel composition also can possess superior mechanical properties, compared to the 40/60 Pb-Sn composition, and readily wets copper.

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### Field of the Invention

This invention relates to Pb-free solder, and to an article comprising the solder.

### Background of the Invention

Solder bonding is a critical step in many industrial processes, e.g., in interconnection and packaging of electronic devices. The most widely used solder is the near eutectic Pb-60% (by weight) Sn alloy. However, due to the toxicity of lead (Pb), there is currently substantial interest in Pb-free substitute solder compositions. Some such compositions are known, (see, for instance, W.B. Hampshire, Electronic Materials Handbook Vol.1, Packaging, ASM International, Metals Park, OH, 1989, p.633).

However, known Pb-free solder compositions have melting temperatures that differ significantly from that of the standard Pb-Sn solder, and have not found significant use in, e.g. electronic packaging. It is common practice in electronic packaging to solder the various levels of the package with different solders of different melting points, selected so that the soldering of each successive level does not inadvertently melt the previously soldered level. Thus, use of a substitute solder having a melting point that differs substantially from that of the solder that is being replaced might require re-design of the packaging operation (a very expensive proposition), or else could cause problems in manufacturing sequences, efficiency, and/or yields. In view of the strong reasons for avoiding Pb-based solder, it would be very desirable to have available a Pb-free solder composition having a melting temperature close (e.g., within  $\pm 10^\circ\text{C}$ ) to that of the standard 40/60 Pb-Sn solder, and having other characteristics (e.g., strength, wettability, creep resistance) that make it suitable as a substitute solder for the standard Pb-based solder. This application discloses such a composition.

### Brief Description of the Drawings

FIG. 1 compares creep deformation of samples of Pb-60%Sn, Sn-5%In-9%Zn, and Sn-10%In-9%Zn, respectively; and

FIG. 2 shows solderability data measured by the wetting balance test.

### The Invention

In a broad aspect the invention is embodied in an article that comprises an essentially Pb-free solder composition having a melting temperature that is close to (desirably within  $\pm 10^\circ\text{C}$ ) that of conventional eutectic or near-eutectic Pb-Sn solder. By "melting temperature" we mean herein the liquidus temperature.

More specifically, the Pb-free composition according to the invention comprises Sn (at least 70, typically at least 80 weight %), Zn (between 3 and 15 weight %, preferably between 6 and 10 weight %), and an amount of In that is effective for causing the composition to have a melting temperature that is at least  $5^\circ\text{C}$  lower than the melting temperature of an otherwise identical, In-free comparison composition. Preferably the In content is selected to yield a melting temperature within  $\pm 10^\circ\text{C}$  of the melting temperature (approximately  $183^\circ\text{C}$ ) of 40/60 Pb-Sn solder and is typically in the range 1-15, preferably 3-10 weight %. The major constituent of the remaining portion of the composition is Sn. Optionally, compositions according to the invention can contain Bi and/or Sb, with the range of the former being 0-10 (preferably at most 5) weight %, and the range of the latter being 0-5 (preferably at most 3) weight %.

Compositions according to the invention not only can have a desirable melting temperature but, quite surprisingly, can have high strength (as expressed by the room temperature ultimate tensile strength or UTS, and/or room temperature 0.2% offset yield strength or YS) and creep resistance, as well as good wetting properties. More specifically, preferred compositions have at least 10% higher UTS and/or YS than 40/60 Pb-Sn, and at least 100% higher creep resistance than 40/60 Pb-Sn, with wetting ability comparable to that of 40/60 Pb-Sn.

Addition of optional Bi will typically result in a somewhat lower melting point whereas, depending on the specific alloy composition, addition of optional Sb will either have little effect on the melting temperature or raise the melting temperature somewhat. However, we have discovered that addition of Bi and/or Sb can result in a refined alloy microstructure and reduced tendency for the formation of undesirable lower melting temperature phases.

Alloys according to the invention optionally may also comprise minor amounts (typically at most 10 weight % in the aggregate) of elements such as Ag, Au, or Cu, added for various purposes such as increasing the solder strength, or further improving wetting behavior on certain surfaces. The desirable amounts of each of these optional constituents are 0-5, preferably at most 2, weight %. Minor amounts of other elements may also be used for a variety of reasons, as is in general known to those skilled in the art. The total amount of optional elements present will typically be at most 15 weight %.

Compositions according to the invention may be prepared by any of a number of known techniques. Exemplary techniques are melting of a mixture of elemental or partially alloyed metals, preferably in an inert atmosphere, deposition of thin or thick films by electrochemical processes such as electroplating, electroless plating and electrophoresis, chemical vapor deposition, evaporation and sputtering.

Compositions according to the invention may be shaped, by any appropriate method, into articles in the form of wires, ribbons, bars or preforms. They can also be incorporated in the form of a powder into solder paste or cream. Solder according to the invention can be used in the manufacture of articles (e.g., surface mounted circuit boards or laser chips solder-bonded to a sub-mount), utilizing known techniques such as wave soldering, dip soldering, or laser soldering. Alternatively, reflow soldering of solder paste, or deposited and patterned solder layers can also be used.

For manufacturability reasons it is frequently desirable that the solder should wet the relevant surface (e.g., copper) within about 2 seconds. Preferred compositions according to the invention have this ability.

Wetting can generally be further improved by use of an inert (e.g., N<sub>2</sub>) or reducing (e.g., forming gas) atmosphere, or by carrying out the soldering operation under a blanket of oil (e.g., propylene glycol).

## EXAMPLES

### Example 1

A Pb-60 wt% Sn binary alloy was prepared from high purity, elemental Pb and Sn. The alloy was melted within a quartz tube having an inside diameter of 14 mm under argon atmosphere, held at 800°C for 8 hours, and furnace-cooled. The resulting ingot was swaged to 3.7mm diameter, remelted within 4mm inner diameter quartz tubes in an argon atmosphere at 300°C for 5 minutes, and then cooled to room temperature. The thus produced rods were then machined into tensile specimens with a 0.5-inch gauge length and 0.120-inch gauge diameter. Tensile tests were performed at room temperature at a strain rate of  $1.67 \times 10^{-3} \text{ sec}^{-1}$ . The 0.2% offset yield strength (YS) was approximately 4500 psi and the ultimate tensile strength (UTS) was approximately 5000 psi. The melting temperature of the alloy was approximately 183°C. Sn-9 weight %Zn-5 weight %In ternary alloy tensile specimens were prepared and tested in substantially the same manner as described above. The results were as follows: the YS was approximately 8000 psi, the UTS was approximately 9000 psi, and the melting temperature was approximately 188°C. No detectable amount of undesirable phases with lower melting temperatures was found.

### Example 2

Sn-9 weight %Zn-10.0 weight %In ternary alloy specimens, prepared in substantially the same manner as in Example 1, had a melting point of approximately 178°C.

The alloy compositions of examples 1 and 2 were subjected to creep testing at 100°C, under a 1000 psi

compressive load. FIG. 1 shows exemplary results of these tests, with numerals 10 and 11 pertaining, respectively, to the inventive compositions of examples 1 and 2, respectively, and numeral 12 pertaining to the prior art Pb-Sn composition. The dramatic improvement in creep resistance is evident.

FIG. 2 shows exemplary data on wetting force on copper, obtained at 245°C in air, using a commercially available (London Chemical Co., Bensenville, Illinois 60106) neutral organic acid flux (NF 3000). The data were obtained by a standard test, generally referred to as the wetting balance test. See, for instance, "A Scientific Guide to Surface Mount Technology", C. Lea, Electrochemical Publications, Ltd., (1988), especially pp. 353-361. In FIG. 2, reference numerals 20 and 21 pertain to a prior art 91/9 weight % Sn-Zn eutectic alloy and the inventive composition of Example 1, respectively, and numeral 22 to the prior art Pb-Sn composition. As can be seen from FIG. 2, the composition according to the invention wets copper, substantially as well as the prior art Pb-Sn composition does, and substantially better than the prior art Sn-Zn composition. More specifically, preferred compositions achieve maximum wetting force in less than 2 seconds, with the maximum wetting force being at least 50% of that of 40/60 Pb-Sn solder at the same conditions (including use of an inert or reducing atmosphere and a conventional low solid flux, or submerged under oil).

## Claims

1. An article comprising an essentially Pb-free solder composition comprising at least 70 weight % tin (Sn) and between 3 and 15 weight % zinc (Zn); associated with the composition being a melting temperature; Characterized In That the composition further comprises an amount of indium (In) effective for imparting to the composition a melting temperature that is at least 5°C lower than the melting temperature of an, otherwise identical, In-free comparison composition.
2. An article according to claim 1, the composition comprising at least 80 weight % Sn, 6-10 weight % Zn, 3-10 weight % In, with the amount of In furthermore selected such that the melting temperature of the composition is in the range  $183^\circ\text{C} \pm 10^\circ\text{C}$ .
3. An article according to claim 2, wherein the composition consists essentially of Sn, Zn and In.
4. An article according to claim 2, wherein the composition comprises one or both of Bi and Sb in an individual amount of at most 10 and 5 weight %, respectively.

5. An article according to claim 2, wherein the composition further comprises at least one element of the group consisting of Bi, Sb, Cu, Ag and Au, with Bi being present in an amount of at most 10 weight %, and the other elements of the group being present in individual amount of at most 5 weight %, and with the total amount of elements of the group being at most 15 weight %. 5
6. An article according to claim 2, wherein associated with the composition is a room temperature ultimate tensile strength (UTS), a room temperature 0.2% offset yield strength (YS), and a creep strain at 100°C, and wherein one or both of UTS and YS are at least 10% larger than the UTS and YS of a 40/60 weight % Pb-Sn composition. 10 15
7. An article according to claim 6, wherein furthermore said creep strain is at most 50% of the corresponding creep strain of said Pb-Sn composition. 20
8. An article according to claim 2, wherein associated with the composition is a wetting force at 245°C in air on copper, and wherein maximum wetting force is attained in a time less than 2 seconds and is at least 50% of the maximum wetting force attained under the same conditions with 40/60 weight % Pb-Sn. 25 30
9. An article according to claim 1, wherein the article is a solder paste, cream, preform, wire, ribbon or bar. 35

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FIG. 1

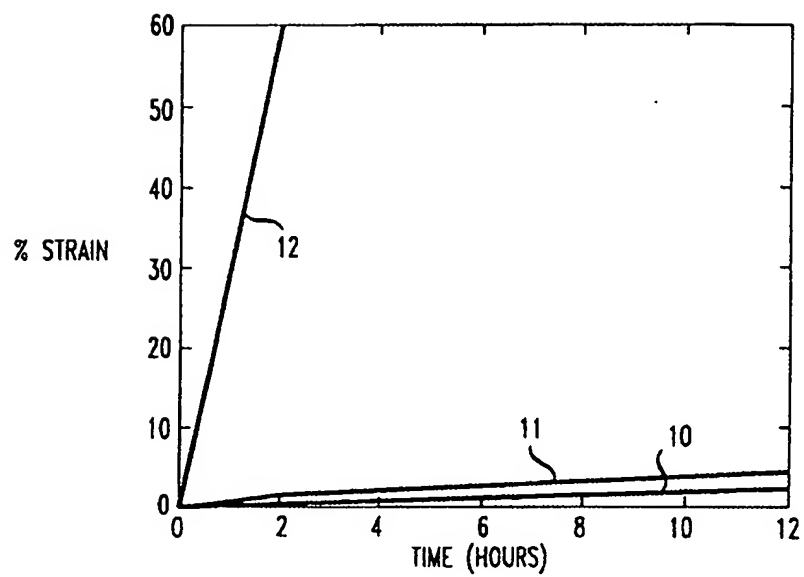
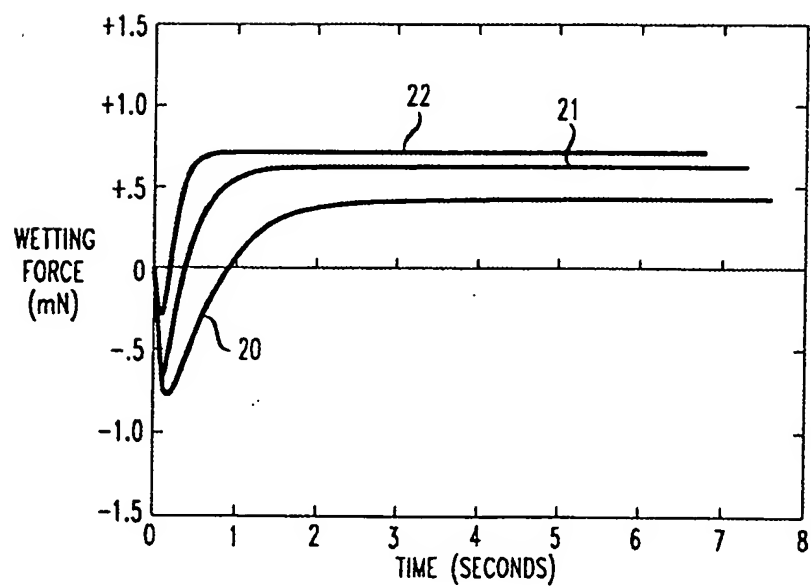


FIG. 2





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 94 30 2785

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	GB-A-131 299 (S.A. DES LAMINOIRS ET CABLERIE) ---		B23K35/26 C22C13/00
A	DE-C-806 820 (FA. G. RAU) ---		
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 486 (M-1038) 23 October 1990 & JP-A-02 197 396 (MITSUBISHI CABLE IND LTD) 3 August 1990 * abstract *		
A	WELDING JOURNAL., vol.71, no.10, October 1992, MIAMI US pages 47 - 49 B.IRVING 'Host of New Lead-Free Solders Introduced' ---		
P,X	US-A-5 242 658 (L.G.STEVENS ET AL) 7 September 1993 * the whole document *	1-3,6-9	
P,X	JOM, vol.45, no.7, July 1993, WARRENDALE US pages 36 - 40 M.MCCORMACK ET AL 'Progress in the Design of New Lead-Free Solder Alloys' * page 39 - page 40 * -----	1-9	TECHNICAL FIELDS SEARCHED (Int.Cl.5)  B23K C22C
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>19 August 1994</b>	Examiner <b>Mollet, G</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			

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